

## Mackenzie River nutrient delivery to the Arctic Ocean and effects of the Mackenzie Delta during open water conditions

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[1] Large rivers have a strong influence on the Arctic Ocean, but little attention has been given to the biogeochemical effect that lake-rich delta floodplains may have on river waters prior to marine discharge. We assessed the effect of the Mackenzie Delta on riverine fluxes of nutrients and organic matter to the Arctic Ocean during the open water period of 2004. Using a new estimate of peak off-channel water storage in the delta floodplain, a two-source mixing model was developed (channel water plus recovery of off-channel water) to estimate the volume-weighted nutrient composition of river water after the off-channel water was recovered from the delta during the hydrograph recession period. Results with the delta effect included (i.e., with recovery of off-channel water) relative to results with the effect omitted (i.e., analogous to historical monitoring upstream of the delta) show particulate levels were 10–18% lower, but enriched in organic content (POC:TSS, PN:TSS, PP:TSS) by 75–280%; dissolved inorganic nutrients were lower ( $\text{NO}_3^-$  14%; SRP 14%; SRSi 5%) except for ammonium (10%); and dissolved organic matter was higher (DOC 15%; DON 62%; DOP 239%). The resulting nutrient quality (C:N:P stoichiometry) was more enriched in carbon (TOC:TP) by 79% and in nitrogen (TN:TP) by 77% relative to phosphorus. Model results were compared against nutrient measurements throughout the delta channel network taken three times over this same period, and differences from upstream to downstream matched reasonably well to the model, though they also suggested the delta effect may be more complex than represented by the model. Our results generally indicate the Mackenzie Delta has an important effect on the magnitude and quality of riverine particulates and nutrients prior to entering the sea. Such an effect has not been quantified in prior work and is likely to be important in other arctic rivers with lake-rich deltas. Our enhanced sampling of the high-discharge period during early hydrograph recession has also better captured the detailed composition of C, N, and P constituents in the river water, ultimately leading to improved estimates of nutrient levels and overall nutrient quality for the open water period that differ appreciably from prior observations on the Mackenzie River.

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### 1. Introduction

[2] Arctic Ocean river inflows are higher per basin volume than other oceans and this has important implications for coastal sea ice formation, open water optical properties and nutrient supply to marine food webs [Aagaard and Carmack, 1989; Gibson *et al.*, 2000; Holmes *et al.*, 2001; Carmack *et al.*, 2004]. Potential climatic warming effects on the arctic hydrosphere have driven

significant recent research to improve the understanding of riverine nutrient fluxes to the Arctic Ocean [Holmes *et al.*, 2000; Lammers *et al.*, 2001; Peterson *et al.*, 2002; Garneau *et al.*, 2006]. The Mackenzie Shelf is strongly influenced by the Mackenzie River and is within a region expected to warm significantly [Rouse *et al.*, 1997; Moritz *et al.*, 2002; Carmack *et al.*, 2004]. Thus understanding of Mackenzie nutrient fluxes to the coastal ecosystem needs to be improved. Several estimates of riverine nutrient fluxes to the Mackenzie Shelf are presently available [Telang *et al.*, 1991; Macdonald *et al.*, 1998; Dittmar and Kattner, 2003; Environment Canada, EcoAtlas, Version 2001\_1\_601\_AR2, CD-ROM, 2001; hereinafter referred to as Environment Canada, 2001]; however, there are three limitations to the existing data sets.

[3] First, historical mass flux estimates from the Mackenzie do not appropriately account for ice breakup effects

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during annual snowmelt-related high flows in spring. During ice breakup in arctic rivers, channel cross sections become filled with varying amounts of moving and jammed ice, which compromise discharge-water level relationships. For such periods, discharge can only be estimated via indirect techniques [Rouse *et al.*, 1997; Shiklomanov *et al.*, 2006]. Mackenzie River records indicate ice breakup conditions lasts an average of 30+ d per year with an estimated 19.5% (55.4 km<sup>3</sup>) of annual Mackenzie discharge (284 km<sup>3</sup>) occurring during this period (L. Lesack *et al.*, River water storage in the Mackenzie Delta and recent changes in the timing, duration, and magnitude of river-ice breakup, submitted to *Geophysical Research Letters*, 2008; hereinafter referred to as Lesack *et al.*, submitted manuscript, 2008). On the basis of a floodplain geometry approach independent of channel discharge, temporary storage of river water off-channel in the Mackenzie Delta at average peak water levels is in the range of 26–31 km<sup>3</sup> [Emmerton *et al.*, 2007]. This stored volume is large relative to estimated river discharge during breakup (47–56%) and suggests that discharges during the breakup period could be underestimated (Lesack *et al.* submitted manuscript, 2008).

[4] The second limitation of the Mackenzie data sets is that nutrient chemistry during the rising limb of the annual hydrograph, which generally is also the period of ice breakup, has never been appropriately characterized because of sampling challenges. This period corresponds to the highest rates of sediment transport and nutrient fluxes during the year [Carson *et al.*, 1998, 1999; Finlay *et al.*, 2006]. Representative measurements are crucial for quantifying annual nutrient fluxes to the Arctic Ocean. The importance of the nutrients delivered to the coastal ocean during this period may be more important than the volume of breakup discharge (55 km<sup>3</sup>) suggests because it represents at least 32% of annual discharge during the nonfrozen period.

[5] The third limitation with existing Mackenzie River records is that the majority of nutrient data are based on measurements upstream of the Mackenzie Delta. Fluxes at the lower end of the delta cannot be measured directly because water discharges among the lower distributary channels are not gauged. This discounts effects that the delta may exert on the river borne nutrients during its 100–200 km seaward passage through distributary channels and off-channel lakes and floodplain [Lesack *et al.*, 1998]. Such “delta effects” on riverine nutrient chemistry, to our knowledge, have not been previously assessed for any of the north flowing arctic rivers. In temperate and tropical river systems, analogous “floodplain effects” on annual riverine nutrient fluxes are considered to be minor and are largely ignored [Forsberg *et al.*, 1988; Vandenbrink *et al.*, 1993; Friedrich *et al.*, 2003; Knowlton and Jones, 2003; Maine *et al.*, 2004]. In the Mackenzie Delta, the effect may be substantial because of its lake richness (>45,000 lakes) that allows large volumes of river water to move in and out of temporary storage during rising and falling waters [Emmerton *et al.*, 2007]. Such lake richness is typical of other arctic deltas and is largely caused by the presence of permafrost and thermokarst melting in areas where heat is

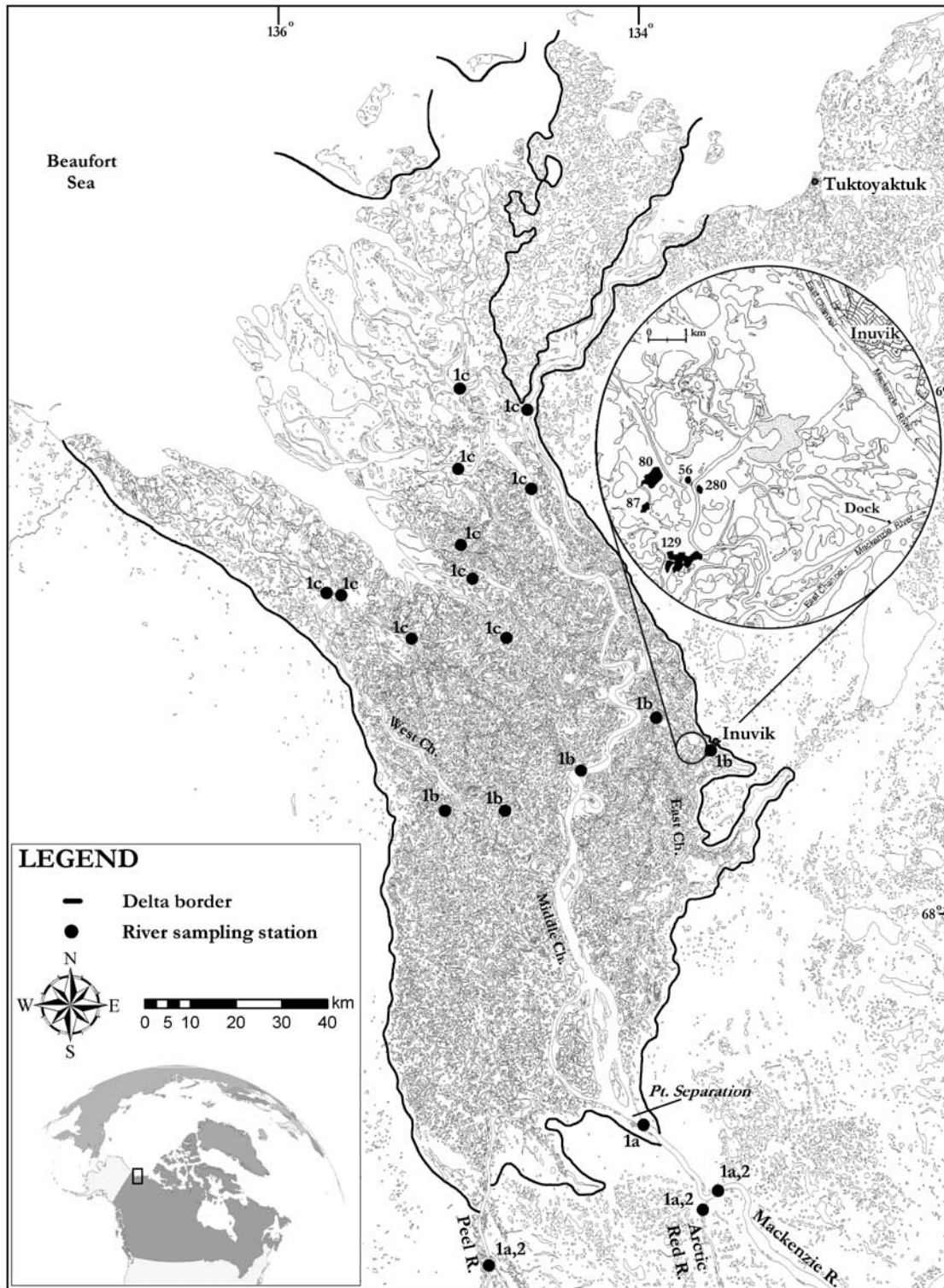
stored in water collecting in topographic depressions [Mackay, 1963].

[6] As a first step in addressing the above limitations, this study focused on quantifying the effect of the Mackenzie Delta on riverine nutrients bound for the coastal Arctic Ocean during the hydrograph recession (i.e., ice-free) period, a time of biological importance in the coastal ocean. To achieve this, a two-source mixing model was developed on the basis of measuring the riverine nutrient flux immediately upstream of the delta (source 1; i.e., analogous to historical monitoring), and estimating the amount of river water that goes off-channel into temporary delta storage at peak annual water level (source 2; i.e., lakes and associated floodplain areas) [Emmerton *et al.*, 2007]. The nutrient content of the stored water was then measured to obtain a mean composition over the recession period, and the nutrient composition that should result from “remixing” river water that did not go into off-channel storage (source 1) with the water coming out of storage (source 2) during the hydrograph recession period was calculated. Comparing results with the delta effect included (source 1 + source 2) against results with the effect omitted (source 1 only), permitted quantification of the “delta effect”. Measurement of nutrient concentrations upstream and downstream in the delta channel network 3 times over the same period permitted assessing how well the model calculations matched observed changes in river water composition. The goals of this paper thus are (1) to assess the hypothesis that nutrients in river water at the lower end of the delta will be substantially modified relative to river water upstream of the delta, because of physical and biogeochemical effects on river water while temporarily stored in the delta; and (2) to improve estimates of Mackenzie River nutrient fluxes during the open water period.

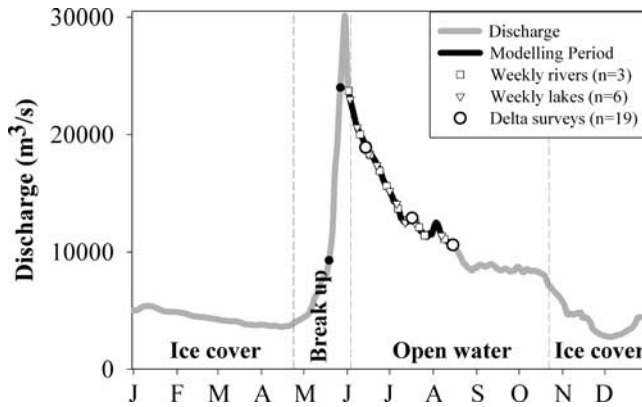
## 2. Methods

### 2.1. Study Area

[7] The Mackenzie Delta (approx. 68–69°N, 134–137°W) lies at the end of the Mackenzie River extending northward to the Beaufort Sea in the western Canadian Arctic (Figure 1). The delta is approximately 200 km long by 80 km wide ranking as the second largest in the circumpolar arctic (approx. 13,000 km<sup>2</sup>; after the Lena). During low-water conditions, its surficial features are characterized by numerous anastomosing channels, wetlands and floodplain lakes that combine to cover almost half of the deltaic plain area [Mackay, 1963; Marsh *et al.*, 1999; Emmerton *et al.*, 2007]. The balance of the delta at this time is dry floodplain material composed of permafrost-influenced organic material, silts and sands. Vegetation across the delta plain consists of species of *Picea*, *Alnus*, *Salix*, *Betula*, *Populus* and *Equisetum* [Mackay, 1963] and tundra species exist north of the treeline. Most lakes are shallow enough to support significant macrophyte communities, which are dominated by *Potamogeton*, *Chara* and *Ceratophyllum* [Squires and Lesack, 2003]. About 90% of the water supplied to the delta is from the Mackenzie River above Arctic Red River with the balance mostly from inflowing Peel (~7%) and Arctic Red (~2%) rivers



**Figure 1.** Mackenzie Delta, N.W.T., Canada. Solid dots indicate sampling locations for each of the river sampling programs: (1) delta surveys, with letters a–c denoting individual transects; (2) weekly river sampling. Six-lake set is shown inset. Further information can be found in Table S3.



**Figure 2.** Mackenzie at Arctic Red River gauging station (10LC014) hydrograph for 2004 with sampling programs superimposed on the graph (solid dots indicate ice-influenced sampling). Note: Lake sampling was performed near Inuvik, N.W.T., downstream of this station and corresponded to the gauging station at Inuvik.

(Figure 1) [Burn, 1995]. The high latitude of the delta region results in 7–8 months of ice cover each year, with peak water levels occurring during spring breakup (Figure 2) in response to basin-wide snowmelt runoff (freshet). Peak water levels are partially controlled by the water amount in the winter snowpack. However, the Mackenzie flows in a northerly direction from areas of relative warmth to colder areas. Melt progresses in the downstream direction and the resulting flood-wave encounters intact ice cover which can cause extensive ice jams and substantially enhanced water level peaks throughout the delta distributary channels [Prowse, 1986]. The period of ice-affected rapidly rising water lasts approximately one month (i.e., early May to early June), then waters generally recede from peak levels after the ice clears, though river flows are still augmented by residual basin snowmelt during the initial recession. Lesack et al. (submitted manuscript, 2008) concluded that flow through the delta fully switches by about 15 July from a freshet runoff regime to a summer regime driven by basin precipitation in liquid form and outflow of stored water from the large lakes in the Mackenzie Basin. The delta lakes are generally small and shallow (<10 ha, <4 m deep), of low conductivity [Fee et al., 1988] and have been classified by lake elevation and connection frequency and duration to adjacent rivers channels [Mackay, 1963; Marsh and Hey, 1989]. No-closure lakes (12% of all lakes, ~60% of total lake area) remain in connection with channels for the entire summer. Low-closure lakes (55%, ~25%) are flooded each spring before disconnecting from the rivers for some portion of the summer. High-closure lakes (33%, ~15%) are not necessarily flooded every spring and never during the summer. This flooding gradient results in biogeochemical, biological and physical gradients across lakes of the delta [Lesack et al., 1998; Squires and Lesack, 2003; Febria et al., 2006].

## 2.2. River Channel–Delta Storage Mixing Model

[8] The river channel–delta storage mixing analysis estimates the lumped effect of mixing channel water, as measured immediately upstream of the delta, with water

draining from the delta lakes and floodplain. Two flux quantities are needed to estimate this effect. The riverine nutrient flux assuming no delta exists downstream of the three inflow rivers, can be defined as

$$\text{FND} = V_r * C_r + V_f * C_f \quad (1)$$

[9]  $V_r$  and  $V_f$  are the volumes of upstream river discharge during the rising and falling water period respectively, while  $C_r$  and  $C_f$  are volume-weighted mean nutrient concentrations of these rivers during the rising and falling water period. The rising water versus falling water periods have been partitioned because of sampling challenges associated with the rising water phase and because of known differences in nutrient composition between stages [Lesack, 1993]. The riverine nutrient flux with the downstream effect of the river delta included can then be defined as

$$\text{FWD} = (V_r - V_o) * C_r + V_f * C_f + V_o * C_o \quad (2)$$

[10]  $V_o$  is the volume of river water that temporarily moves off-channel into the delta lakes and associated floodplain (3 lake classes) up to the point of peak water level and  $C_o$  is the volume-weighted mean concentration of water draining from off-channel areas that remixes with delta channels. Whereas FND is equivalent to what riverine nutrient fluxes should be if the delta effect is ignored, fluxes previously published for the Mackenzie have typically been estimated as

$$\text{FPP} = (V_r + V_f) * C_f \quad (3)$$

[11]  $C_f$  generally corresponds to measurements during the ice-free period. Since appropriate measurements are still not available to accurately estimate  $C_r$ , we have restricted our present comparison of FND versus FWD to the hydrograph recession period. We thus define our comparison fluxes as follows:

$$\text{FND}_f = V_f * C_f \quad (4)$$

$$\text{FWD}_f = V_f * C_f + V_o * C_o \quad (5)$$

[12] Because the recovery of delta floodplain water ( $V_o$ ) represents additional water volume to  $V_f$  during the recession period, the additional water will translate into a larger nutrient flux. Thus we have compared the two following volume-weighted mean concentrations as a measure of the delta effect:

$$\text{CND} = (V_f * C_f) / V_f \quad (6)$$

$$\text{CWD} = (V_f * C_f + V_o * C_o) / (V_f + V_o) \quad (7)$$

[13] CND and CWD were estimated over the period from 3 June to 15 August 2004, representing the time from flood peak until most of the stored water had been recovered. Measurement information related to model variables and a calculation example are given in Tables 1a and 1b.

**Table 1a.** Sampling and Data Information and Integration Into the Mixing Model Using Total Dissolved Organic Carbon as an Example; No Delta Effects (CND)<sup>a,b</sup>

|  | Model Component | Mackenzie River | Arctic Red River | Peel River | Total  |
|--|-----------------|-----------------|------------------|------------|--------|
| Inflowing river flow volume, km <sup>3</sup> | Vf              | 94.1            | 1.6              | 5.7        | 101.5  |
| Mean concentration, $\mu\text{mol L}^{-1}$   | Cf              | 324             | 159              | 140        | -      |
| River mass flux, mol $\times 10^6$           | Vf $\times$ Cf  | 30,505          | 261              | 802        | 31,568 |

<sup>a</sup>Volume-weighted mean concentration,  $\mu\text{mol L}^{-1}$ : 311.

<sup>b</sup>Dates: 3 June to 15 August 2004. Vf: summed volumes of three delta-inflowing rivers during the modeling period (Water Survey of Canada, HYDAT CD-ROM, version 2004 2.04, software, 2005). Cf: particulate, DOM, and dissolved constituent mean concentrations of inflow rivers during the modeling period. Mackenzie River above Arctic Red River: weekly sampling from 2 June to 9 August 2004. Arctic Red and Peel rivers: weekly sampling from 10 June to 9 August 2004. Vo: summed volumes of drainage from each lake class during modeling period. From *Emmerton et al.* [2007], delta lake drainage model based on 2004 delta peak water level of 5.519 m asl. Co: particulate, DOM, and dissolved constituent mean concentrations of an Inuvik region six-lake set (Figure 1) during the modeling period. No-closure (lakes 129, 80), low-closure (87, 280), and high-closure (56, Dock) lakes measured weekly from 3 June to 7 August 2004.

[14] Given that Vo represents water that moved into storage during the rising water phase, the “delta effect” we have quantified here (CWD/CND) is conceptually analogous to a correction coefficient for the restricted period of the hydrograph recession, rather than a measure of net nutrient balance for the delta which would require extending this analysis through the rising water phase. Though results are restricted to the hydrograph recession, this period is important in itself because it is a time of biological importance in the coastal ocean [*Garneau et al.*, 2006].

### 2.3. Upstream-Downstream Channel Nutrient Comparison

[15] A supplementary nutrient comparison was performed to help assess model results. Upstream to downstream nutrient concentration changes through the delta channels were evaluated through delta-wide sampling surveys performed 3 times over the falling water period of 2004 (14 June, 17 July, and 15 August; Figures 1 and 2). Three transects (19 sites) based on work by *Carson et al.* [1999] were chosen to synoptically sample the inflow rivers at the delta head (Figure 1, number 1a), and to sample the major distributary channels at the middelta point (Figure 1, number 1b) and near the delta mouth (Figure 1, number 1c). All river sites were measured for conductivity to ensure that saltwater influences were nil, particularly across the delta mouth transect.

### 2.4. Water Sample Collection

[16] River water (Cf) was sampled from the Mackenzie, Arctic Red and Peel rivers as near-shore, surface grabs (Figure 1, number 2). Samples were directly collected into clean, site-rinsed 2 L LDPE bottles, being careful not to collect stirred bottom sediments. All samples were then

stored in dark and cool conditions during transit to the laboratory. Delta lake water (Co; six-lake set, Figure 1, inset) was collected midcolumn by boat using a clean, vertically oriented Van Dorn sampler. Delta lakes have well-mixed water columns after ice out [*Lesack et al.*, 1991], thus midcolumn samples were taken as representative of the entire lake and floodplain. Dock Lake samples were collected as surface grabs from shore and this lake was the only of the six-lake set not to flood during 2004. All samples were transferred onsite to clean, site-rinsed 2 L LDPE bottles and stored in cool and dark conditions during transit to the laboratory. Delta-wide channel survey samples were collected approximately midchannel as surface grab samples using clean, site-rinsed 1 L HDPE bottles. During the 5-h helicopter survey period, samples were stored in cool and dark conditions until return to the laboratory.

### 2.5. Analytical Methods

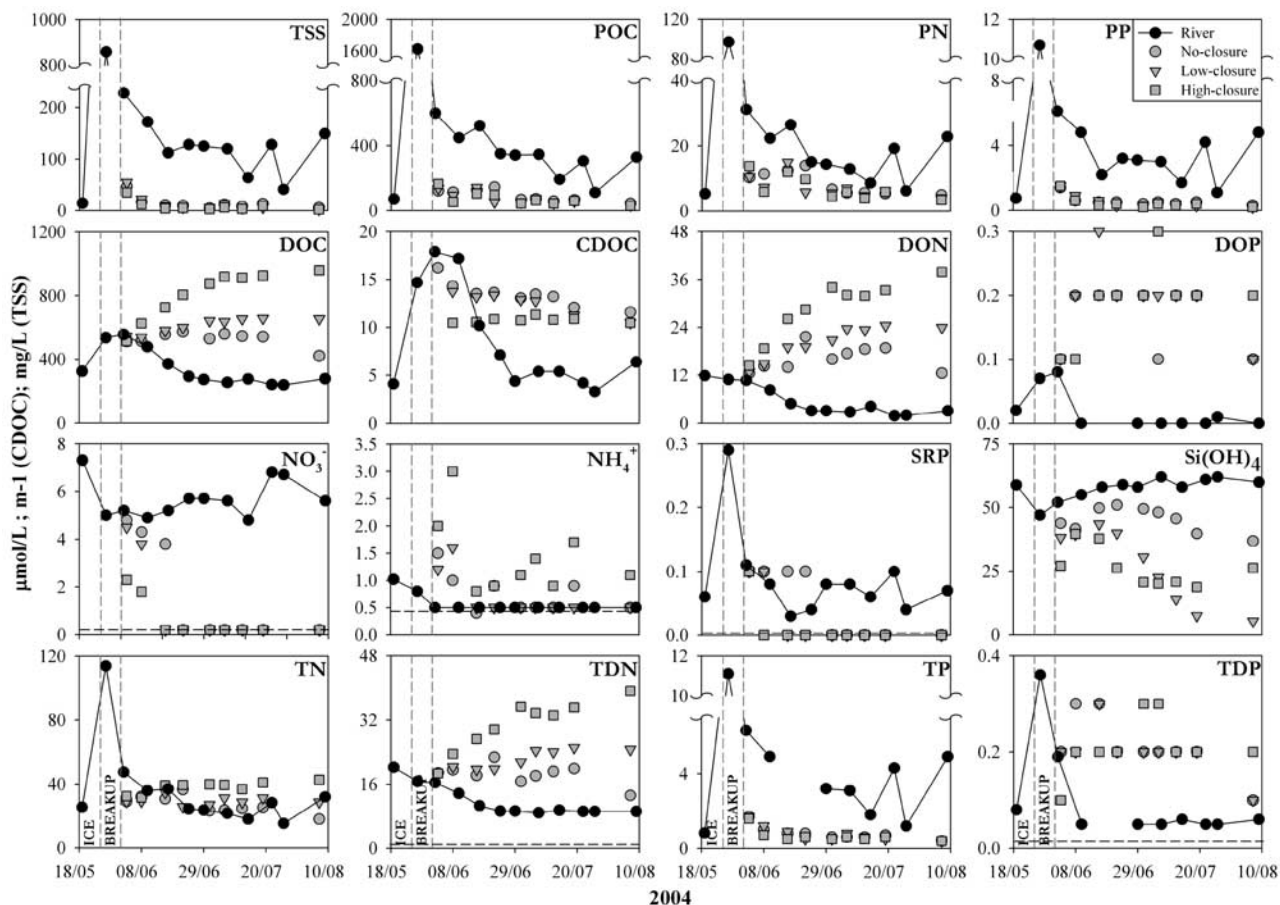
[17] Upon return from the field, all samples were well mixed and passed through Whatman GF/C filters. GF/C filtration was chosen to be consistent with historical delta data sets and prior testing of GF/C filtration versus filters with smaller pore sizes has shown negligible differences in nutrient and particle analyses in this system. Sample filtrate was partitioned for separate analyses into clean 60 mL or 125 mL HDPE bottles rinsed with filtrate. Samples were partitioned for: nitrate ( $\text{NO}_3^-$ ) and common anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ); soluble reactive silica (SRSi); total dissolved organic carbon (TDOC); colored dissolved organic carbon (CDOC); total dissolved nitrogen and phosphorus (TDN, TDP); and soluble reactive phosphate and ammonium (SRP,  $\text{NH}_4^+$ ). Subsamples for CDOC analysis were further passed through Millipore<sup>®</sup> nitrocellulose 0.22  $\mu\text{m}$  filters to ensure all submicron sized particles capable of irradiance scattering

**Table 1b.** Sampling and Data Information and Integration Into the Mixing Model Using Total Dissolved Organic Carbon as an Example; With Delta Effects (CWD)<sup>a,b</sup>

|   | Model Component               | No-Closure Lakes | Low-Closure Lakes | High-Closure Lakes | Total  |
|---|-------------------------------|------------------|-------------------|--------------------|--------|
| Lake outflow volume, km <sup>3</sup>          | Vo                            | 19.3             | 5.1               | 0.5                | 24.9   |
| Mean concentration, $\mu\text{mol L}^{-1}$    | Co                            | 528              | 612               | 807                | -      |
| Lake mass flux, mol $\times 10^6$             | Vo $\times$ Co                | 10,172           | 3114              | 388                | 13,673 |
| Total flow volume from delta, km <sup>3</sup> | Vf+Vo                         | -                | -                 | -                  | 126.3  |
| Lake+river mass flux, mol $\times 10^6$       | Vf $\times$ Cf+Vo $\times$ Co | -                | -                 | -                  | 45,241 |

<sup>a</sup>Volume-weighted mean concentration ( $\mu\text{mol L}^{-1}$ ): 358.

<sup>b</sup>See footnote for Table 1a.



**Figure 3.** Weekly six-lake set and Mackenzie River at Arctic Red River nutrient concentrations measured during the 2004 open water season. “Ice” indicates river ice cover conditions and “Breakup” indicates the period of ice breakup in the river. Horizontal dashed lines indicate analytical detection limit.

at ultraviolet wavelengths were removed prior to spectrophotometric scans. Total suspended solids (TSS) and particulate nutrients (POC, PN, PP) were measured using precombusted GF/C filters (16 h at 500°C) and were oven-dried at 100°C for 24 h afterward. Total and dissolved organic measures of nitrogen, phosphorus and carbon were calculated via other measures (TN = PN + TDN; TP = PP + TDP; TOC = POC + TDOC; DON = TDN – NO<sub>3</sub><sup>-</sup> – NO<sub>2</sub><sup>-</sup> – NH<sub>4</sub><sup>+</sup>; DOP = TDP – SRP). For DON calculations, NO<sub>2</sub><sup>-</sup> was assumed to be zero because our prior work established it is negligible in this system. All components were analyzed following standard methods as outlined by *Strickland and Parsons* [1972] and *Stainton et al.* [1977] and further analytical information is provided in Table S1.<sup>1</sup>

### 3. Results

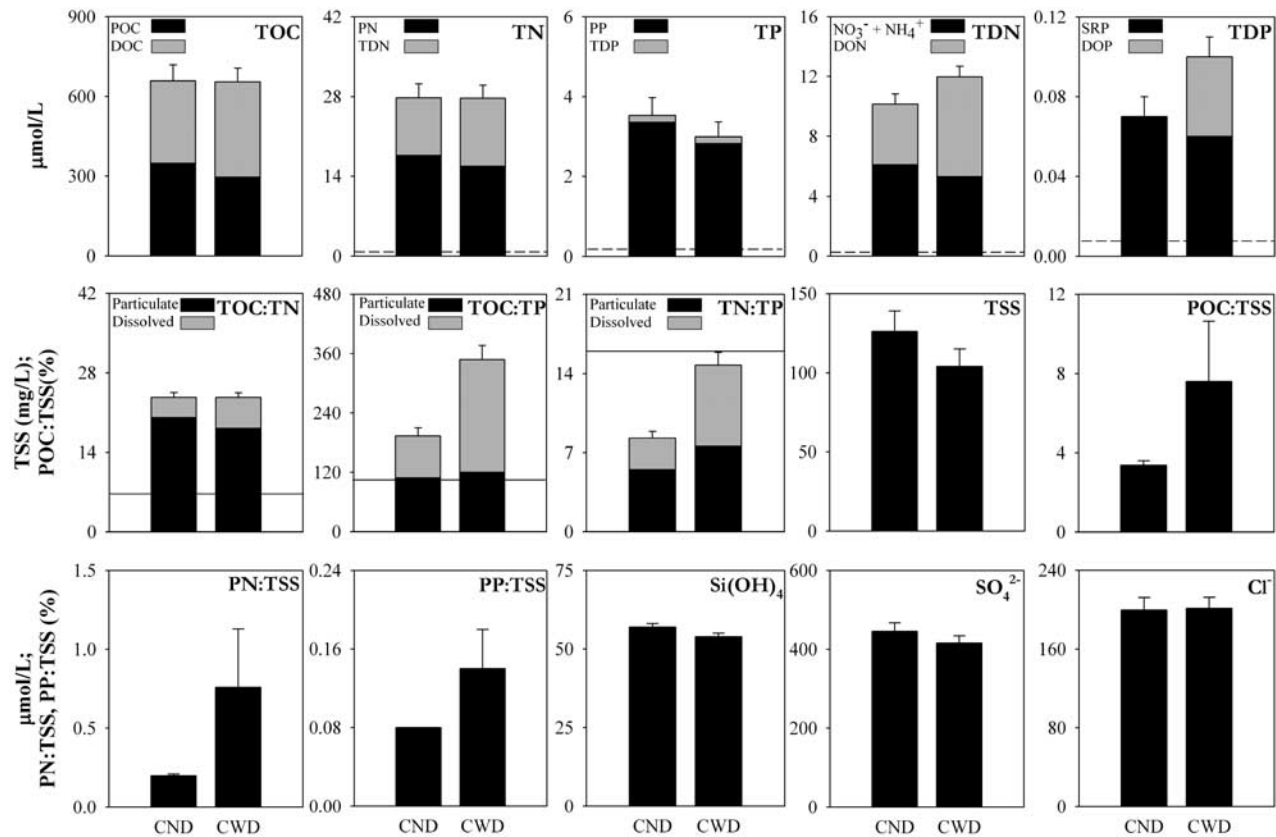
#### 3.1. Seasonal Nutrient Patterns of the Mackenzie River

[18] Sampling of rivers and delta lakes was initiated just after peak discharge and water levels in the delta and was

representative of the majority of the hydrograph recession period (Figure 2). One under-ice sample during the early breakup (via auger) and one sample from river shore openings during the latter breakup period were also obtained to gain some understanding of rising limb nutrient characteristics, though these measures were not used in the model. The results do, however, indicate that nutrient levels during the rising limb are likely substantially different than the recession phase. Nutrient results from the Mackenzie (Figure 3) followed the general pattern observed in other arctic rivers [*Dittmar and Kattner*, 2003]. Particulates and DOM were high near peak discharge and sharply declined after the flood. A rise in water level unrelated to discharge affected nutrient concentrations in the river channels and lower-elevation lakes at the end of July in response to a coastal storm surge from the Beaufort Sea coast. DOP was low throughout the year showing only small increases during the flood peak. Excluding ammonium and SRP, which were variable, inorganic nutrients were at a minimum during peak flooding and generally increased afterward. TN and TP reflected the dominance of particulates within their measures while TDN and TDP were variable throughout the year, representing a composition split between organic and inorganic forms.

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2006GB002856.





**Figure 4.** Delta channel–storage mixing model results for various measures. CND denotes “no delta” concentrations while CWD denotes “with delta” concentrations. Horizontal lines denote the Redfield ratio, and horizontal dashed lines indicate analytical detection limits. Error bars indicate  $\pm 1$  S.E., based on sample sizes, but not complete error propagation (see section 3 for details).

also indicated but these may not be significant. Conversely, the delta may have been a source of ammonium, possibly increasing river levels by 10% (see prior text on detection limit), while chloride was conservative in behavior.

[23] TP declined by 14% when the delta effect was included, since the particulate fraction was dominant over the dissolved fraction. On the other hand, TN showed no net effect because the particulate fraction and dissolved inorganic (mainly  $\text{NO}_3^-$ ) fractions were removed from water off-channel while the dissolved organic fraction was augmented by a comparable amount. TOC also showed no net effect since a decline in POC was offset by increases of TDOC.

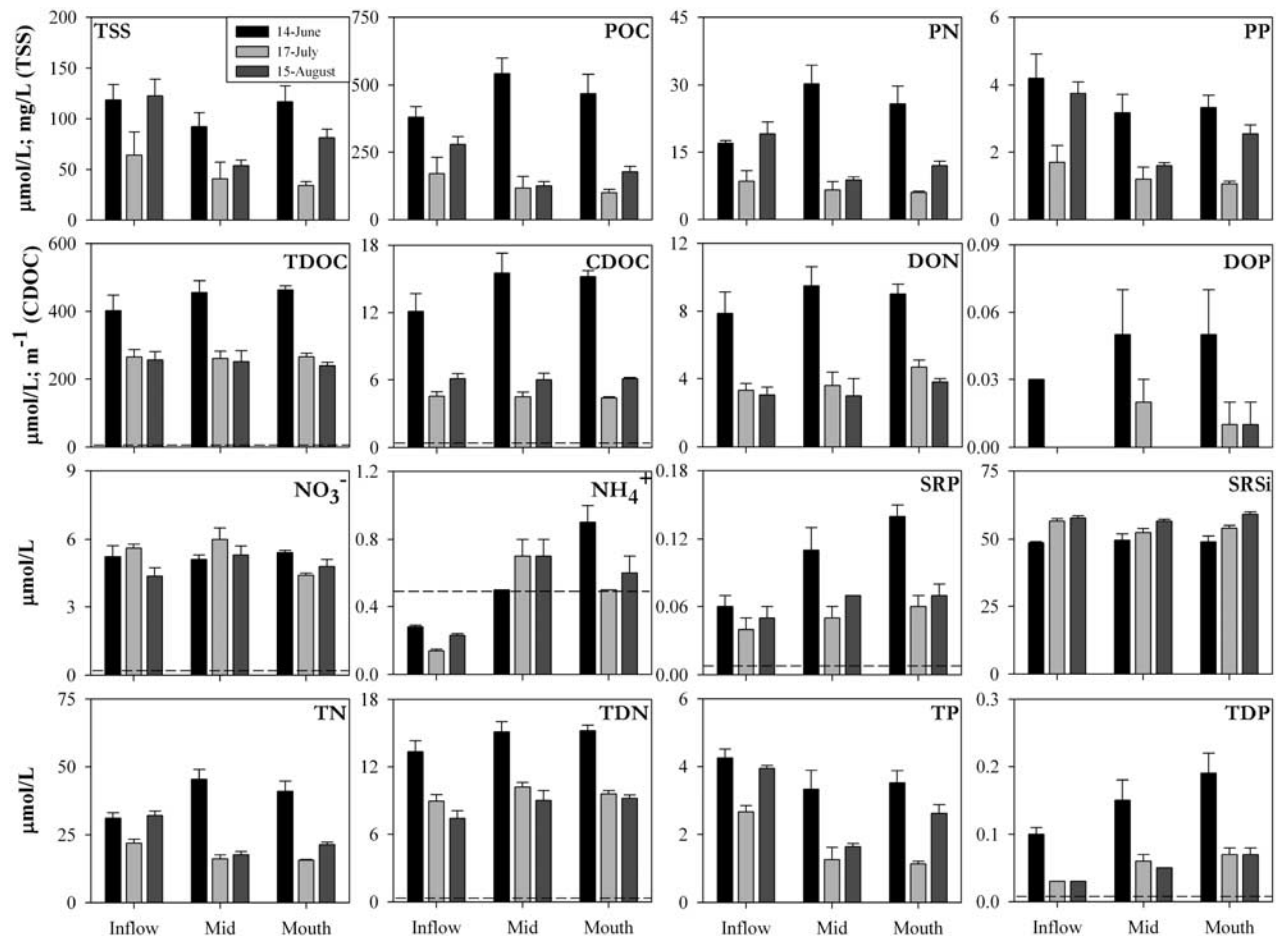
[24] Whereas the ratio of TOC:TN showed no net change when the delta effect was included, TOC:TP and TN:TP both changed substantially. The net effect of these changes indicates river water nutrient quality is richer in C and N, and that N:P is close to the Redfield ratio upon discharge to the sea [Redfield, 1958]. Most of the change in the total C:N:P ratios are a result of changes in the dissolved fraction. However, PN:PP appeared to show substantial enrichment of N when the delta effect on river water is included.

### 3.3. Downstream Nutrient Changes in Delta Channels

[25] Upstream-downstream nutrient comparisons from the delta-wide sampling are shown in Figure 5. These results are largely consistent with the estimates from the mixing model (Table 2, % change), although they also suggest the delta effect may be weaker and more complex than indicated by this model. Two constraints on these upstream-downstream results are that the comparisons are qualitative because water discharges are not available to weight the observed concentrations in the lower-delta channels, and that the strength of the potential delta effect will diminish as time from the discharge peak lengthens. Thus the timing of the measurements is important (Figure 2). Since the first channel survey was substantially closer to the discharge peak than the latter two surveys, we expect the delta effect to be stronger at that time, and thus consider that survey time to be a better test of the delta effect than the latter two.

[26] In all three surveys, TSS and PP each declined in concentration at downstream channel locations relative to the delta inflow point. On the other hand, POC and PN increased downstream from the inflow point during the June survey, but then switched to a pattern of downstream decline in the latter two surveys. The July 2004 survey showed steady downstream decreases between all sites





**Figure 5.** 2004 delta survey results for particulates, DOM, dissolved inorganic nutrients, and composite measures. Horizontal dashed lines indicate analytical detection limit. Error bars denote  $\pm 1$  S.E., based on sample sizes only because channel discharges in the middle and lower delta are not presently known (see section 3 for details).

among each measure whereas nearly all measures in the August survey showed a modest increase from the middelta to the lower-delta transect. The switching pattern for POC and PN is consistent with model results (Table 2) that indicate an overall decline in average POC and PN concentrations over the full observation period as a result of the delta effect, but a strong enhancement in the ratios of POC:TSS and PN:TSS. The June pattern of POC and PN is evidence that the strongest ratio enhancement occurred earlier in the recession period, whereas the July and August surveys are consistent with the overall effect being to lower the average concentrations.

[27] Downstream increases in DOM relative to the delta inflow point were strong for DOP. However, downstream increases of other DOM constituents (TDOC, CDOC, DON) appeared relatively weak, with the exception of DON in the latter two surveys where notable increases occurred from the delta inflow point to the lower delta.

[28] Whereas basic principles and the results of the mixing model analysis indicate that inorganic nutrients to some degree should to be removed from the river water

while stored in the delta, there was little evidence of such removal in the upstream-downstream observations. There was possible indication of a minor reduction in  $\text{NO}_3^-$  downstream from the delta inflow point during the July and August surveys, and minor reduction in SRSi in the June and July surveys. By contrast there were downstream increases in ammonium during all three surveys and in SRP during the June survey. Sulfate and chloride concentrations (not shown in Figure 5) showed no evidence of downstream changes in concentration through the delta during the surveys.

[29] Downstream changes in TDN relative to the delta inflow point showed small increases representative of the two-thirds DON composition of TDN across all surveys. Nitrate represented the balance of TDN with ammonium making a relatively small contribution. TN increased downstream from the delta inflow point during the June survey mainly as a result of increases in PN, which represented 60% of TN. TDP increased downstream from the delta inflow point during the June survey, mainly as a result of increases in SRP. Dissolved phosphorus was generally low

and DOP represented about 20% of all TDP over all delta-wide surveys. TP declined downstream from the delta inflow point, mainly because of the downstream decline in PP. Total organic carbon (not shown in Figure 5) showed minor downstream increases during the June survey, then minor downstream declines during the latter two surveys, in both cases because of the behavior of POC.

[30] Nutrient ratios from delta surveys (not shown) showed considerable downstream increases for TOC:TN and TN:TP across all surveys. The June survey showed increases for PN:PP while latter surveys showed relative stability downstream for all particulate nutrient ratios.

## 4. Discussion

### 4.1. Seasonal Nutrient Patterns

[31] The seasonal pattern of nutrient fluxes in the Mackenzie River is generally consistent with prior reports from large arctic rivers. Nutrient fluxes follow highly seasonal patterns that are primarily driven by snowmelt hydrology [Vorosmarty *et al.*, 2001]. This response contributes to nutrient characteristics that are quite different from world river averages [Meybeck, 1982; Telang *et al.*, 1991; Lara *et al.*, 1998; Gordeev, 2000; Holmes *et al.*, 2001]. Dissolved inorganic nutrients may progress from a maximum in early spring (under ice) if flow is dominated by nutrient-rich groundwater, to a minimum during the spring freshet period because of dilution [Cauwet and Sidorov, 1996; Holmes *et al.*, 2000]. Ammonium is a notable exception to this pattern as spring snow and river ice are relatively high in ammonium and low in oxidized nutrients [Dittmar and Kattner, 2003]. The Mackenzie generally has higher inorganic nutrient concentrations compared to Eurasian rivers [Lobbés *et al.*, 2000] due mostly to basin effects as the Mackenzie Basin is largely undeveloped. One important exception would be SRP, which is often higher in Eurasian rivers with more development pressures. However, levels of inorganic nutrients in arctic rivers are generally among the world's lowest [Meybeck, 1982].

[32] Dissolved organic material and particulates typically increase with flow during the rising limb of the hydrograph [Finlay *et al.*, 2006]. Snowmelt percolating through organic-rich taiga soils [Dittmar and Kattner, 2003] and erosive runoff in associated subbasins are likely the main drivers of this increase during this period. However, the magnitude and timing of these concentrations peaks, in the case of the Mackenzie, have never been appropriately sampled because of the technical challenge of sampling through river ice in the process of breakup. Our single sample of river water from the breakup period suggests levels of DOM, particulates and SRP could be higher during the breakup period than at or after the discharge peak. The discharge recession period has generally been associated with declines in dissolved organic constituents and particulates as discharge declines. Each then progress toward an early winter minimum where groundwaters, depleted in organics and particulates, may dominate channel discharge. The Mackenzie River is generally lower in all DOM measures compared to Eurasian rivers [Lobbés *et al.*, 2000]; however, the reasons for these differences are poorly understood and possibly

hindered by sampling challenges during peak concentrations during spring breakup [Finlay *et al.*, 2006]. The Mackenzie is also enriched in sediments, POC, PN, organic carbon content of particulates and POC:PN ratios [Lobbés *et al.*, 2000]. Inputs to the Mackenzie from several sediment-rich, mountain-sourced rivers such as the Liard River may play an important role in these high concentrations compared to its Eurasian counterparts; however, more study is needed to decipher these trends among arctic rivers. Overall, organic matter content in arctic rivers appears to be among the highest reported in world rivers [Dittmar and Kattner, 2003] while sediment content is variable among arctic rivers.

### 4.2. Effect of the Delta on Mackenzie River Nutrient Fluxes

[33] In principle, the delta effect on fluxes of suspended sediments and dissolved nutrients in the Mackenzie should be qualitatively similar to what has been observed in other rivers. A general pattern is that suspended sediments and inorganic nutrients are stripped out of river water moving off-channel. DOM levels in the floodplain waters subsequently become augmented as autotrophic production is enhanced via improved water transparency and availability of nutrients directly from the river water or extracted from the deposited sediments via macrophytes. However, prior to our results here, the scale of this effect among particulates and dissolved forms, and the degree of biogeochemical transformation occurring while the water is in off-channel storage has not previously been quantified in arctic rivers. The only prior work our results can be directly compared to is the sediment flux results of Carson *et al.* [1999], and an earlier paper by Prowse [1993] where suspended sediment levels were directly measured during the breakup period.

[34] Our model results indicated that net sedimentation from river water during off-channel storage was an important though moderate effect during the period of observation. However, the full extent of deposition was likely underestimated because the analysis was restricted to the discharge recession period only. The mass balance study of Carson *et al.* [1999] estimated about 34% of all sediment delivered to the delta is deposited within delta lakes and channels, in comparison to our model estimate of 18% for the recession period only (TSS, Table 2). Considerable sedimentation into the delta lakes and floodplain likely occurred during the breakup period, when river waters rise rapidly and initially move off-channel. Prior work, based on samples taken from helicopter, has shown suspended sediment levels are considerably higher levels during Mackenzie breakup, relative to the recession period [Prowse, 1993]. Our model results also would have underestimated particulate deposition because in-channel sedimentation was not accounted for, especially in the delta mouth region where depositional rates are high [Carson *et al.*, 1999]. Our results showing enriched organic content of TSS (POC, PN, PP:TSS) when the delta effect is included is fully consistent with the flushing of living and detrital macrophyte and terrestrial plant and soil material back into delta channels during initial lake drainage after flooding. POC

and PN patterns from the upstream-downstream channel survey in June (Figure 5) appear to have captured this flushing effect. Direct evidence of such flushing was also observed during a summer 2004 research cruise where zooplankton tows captured variable types and sizes of macrophyte material in delta channels (A. Casper, unpublished data, 2004).

[35] Our model results also generally showed that DOC, DON, and DOP should be enhanced in river water as it flows through the delta (Figure 4). This is consistent with ongoing work in lakes of the delta, which show high DOM in lake waters are derived from leaching of high-biomass macrophyte communities plus benthic and epiphytic algae [Lesack et al., 1998; Squires and Lesack, 2003]. Other work has shown that floodwaters can acquire significant concentrations of DOC (and inorganic nutrients) via percolating among flooded vegetation and soils around delta lakes [Lesack et al., 1998; see also L. Lesack et al., Ecology of lakes in the Mackenzie River Delta: River ecosystem theory and potential responses to global change, submitted to *Freshwater Biology*, 2008]. This can contribute significant DOM to lake waters that may subsequently drain back to delta channels during falling water. Acquisition of such DOM from areas beyond lake boundaries, however, is limited to the period of direct contact with floodwaters because discharge of soil/groundwater from floodplain soils after floodwaters recede is very limited [Marsh and Lesack, 1996]. DOP through the delta also is generally low in river waters and higher in lakes, similar in pattern to DOC and DON [Lesack et al., 1991]. Our channel network surveys confirmed that DOP levels were indeed enhanced at the downstream end of the delta, as our model results suggested, but this effect was weaker in the cases of DON and DOC. This may have been due to inherent differences between the mixing model, which integrates results over the full observation period, and the channel network surveys, which represent one instant in time. It is also possible in-channel processes, such as adsorption of lake DOM onto river particles [Retamal et al., 2007], were occurring but not represented in our model. Subsequently, increased particle transport during flooding may have proportionally affected DOM changes during the June survey. CDOC followed a similar seasonal pattern as TDOC; however, its level relative to TDOC decreased throughout the season in the various distributary channels of the delta. During the July survey, the levels of CDOC declined downstream through the delta, as might be expected if chromophoric DOC molecules were photobleached while stored in the delta. Ongoing work has shown photobleaching of DOC can be significant in the delta [Febria et al., 2006], with the highest rates occurring near the solstice period when CDOC is relatively high in lake and river waters and irradiance is strongest.

[36] Our model results indicated that river water levels of SRP, nitrate, and silica should be reduced during passage through the delta. These results are consistent with prior work on lakes of the delta that show primary producers [Squires and Lesack, 2003] and aquatic bacteria [Spears and Lesack, 2006] are most typically P-limited, relative to N, and with other work that has directly shown substantial

declines in silica in some lakes over the summer [Lesack et al., 1998]. The upstream-downstream channel surveys showed only weak evidence of downstream declines in nitrate and silica in river water, whereas SRP and ammonium showed downstream increases in the June survey. The nitrate and silica observations can be reconciled by the fact that concentrations of both constituents are relatively high in the river water, and that the primary producers and aquatic bacteria tend toward P-limitation early in the open water season. The ammonium results are fully consistent with our observations in prior work that indicate ammonium concentrations are typically only at trace levels in the river, but is the primary form of recycled N in the lakes and floodplain (Figure 3) [Spears and Lesack, 2006]. We thus expected nitrate to show net uptake and ammonium net release in this investigation. More complicated to interpret is the apparent release of SRP in the June survey. While the aquatic organisms are typically P-limited by the time seasonal primary production takes off, large releases of both SRP and ammonium typically occur in lakes of the delta over the course of the winter under-ice cover [Lesack et al., 1991; Pipke, 1996]. It is plausible such under-lake-ice releases are responsible for the particular results during the June channel survey, whereas our model results yield an integrated result for the entire recession period. An alternative possibility is that the observed downstream enhancement of DOM levels may have stimulated in-channel microbial activity, resulting in releases of SRP and/or ammonium. Bioassays of microbial P debt and N debt in lake waters receiving frequent inputs of river water [Spears and Lesack, 2006], however, have shown that significant net releases of SRP are rare. A second alternative is that in-channel dissociation of SRP from sediment particles may have occurred, particularly toward the mouth [Fox et al., 1985]. Since our channel surveys were kept within the zone of fully freshwater, SRP release via particle dissociation seems less plausible.

[37] Our model results generally indicate that the C:N:P ratios in river water exiting the delta represent a considerably different nutrient quality for organisms on the Mackenzie Shelf than would be inferred from the historical nutrient measurements at the Mackenzie gauging station upstream of the delta. This was generally matched by data from channel surveys, especially during the flooding period when river-floodplain connection was enhanced. An important constraint here is that our corrections for the delta effect are limited to the hydrograph recession period. The full nutrient flux exiting the delta if the breakup period was included would likely be higher in particulate content (see Figure 4), which could result in a higher N:P ratio than our measurements reported here.

#### 4.3. Model Limitations

[38] The results from our mixing model generally showed that the Mackenzie Delta has an important effect on the quantity and quality of nutrients transported to the Beaufort Sea. However, the particular results reported here need to be interpreted with a number of constraints. Significant remaining issues include (1) the precision of the water volume stored in the delta at peak water levels; (2) the degree to

which the delta effect may be stronger if the rising water phase of the hydrograph is included; and (3) the representativeness of the nutrient chemistry of the stored water that remixes with river water.

[39] The precision of the stored water volume is being assessed in ongoing investigations. The six lakes used to estimate the nutrient content of the floodplain water are a well-studied set of lakes [Squires and Lesack, 2003; Spears and Lesack, 2006; Febria et al., 2006] that were fully tracked over the period of investigation. The nutrient levels in these lakes have also compared favorably against broader sets of lakes in the delta sampled in other years, including 40 lakes in the Inuvik area, 81 lakes across the delta from Inuvik to Aklavik and clusters of 12 and 14 lakes respectively in the upper and lower delta [Lesack et al., 1998]. Future work should include more spatially extensive sampling of delta floodplain lakes to improve stored water nutrient estimates. We plan to apply a hydraulic network model that includes ice jam effects on discharge during the breakup period [Blackburn and Hicks, 2003]. This is especially important for evaluating the potential difference of the delta effect during the rising water phase and the recession period, which may be substantial.

[40] Riverine nutrient fluxes can also be improved if our current model is expanded from handling the hydrograph recession as a single lumped effect to providing time-dependent drainage of stored water and nutrients to the delta channels. This is an achievable goal, but requires the capability to estimate the volume of water stored in the delta through the full range of water levels rather than only at peak level [Emmertson et al., 2007]. Stored water drains more rapidly from the delta early during the recession period than later during the recession period, and ideally, the nutrient chemistry of water in the delta should be weighted according to the time-dependent rate of water drainage (not yet known). This limitation has likely caused overestimation of the delta effect for some constituents and underestimation for others, but the present set of results represents our best estimate of the effect until further work is completed. Adding such capability, coupled with enhanced lake sampling, may also resolve observed complexities in the downstream patterns of nutrients in the channel network, such as the switching behavior in downstream patterns of POC and PN from earlier in the recession to later.

#### 4.4. Climate Change Effects

[41] Adding to the complexity of assessing Mackenzie River nutrient fluxes are recent findings that the river and delta system have significantly changed in the past several decades in response to climatic warming. Analysis of water levels has suggested the duration of river ice breakup from just upstream of the delta to the central delta (115 km distance) may have declined over the past 30 years [Lesack and Marsh, 2007]. Moreover, peak annual water levels in the central delta during recent years appear to be earlier, and possibly declining, in contrast to the pre-1986 period where peak levels consistently occurred during a very narrow time window (3 June standard deviation 4 d). Because there has been no detectable change in published Mackenzie dis-

charge over the same time [Peterson et al., 2002; Woo and Thorne, 2003], the cause appears to be a long-term reduction in the severity of ice breakup effects. Our analysis in the present paper is not directly affected because it is based on the actual peak water level that occurred during 2004. However, an implication is that the delta effect may become significantly diminished if long-term peak water levels decline with further climatic warming. In particular, fluxes of dissolved organic matter in river water that appears to be enhanced by the delta effect, may decline. The amount of suspended sediments and inorganic nutrients stripped from river water while stored off-channel in the delta would also decline if the average volume of stored water decreased as a function of declining water level peaks.

[42] A second important finding is that river-to-lake connection times in no- and some low-closure lakes of the delta (accounting for >60% of the delta lake area) appear to have lengthened in response to a significant rise in late summer water levels of delta channels over the past several decades [Lesack and Marsh, 2007]. Over the same period, however, average relative sea level at the coast has risen [Manson and Solomon, 2007] by an amount that is substantially smaller. These enhanced delta water levels, relative to the sea level effect, may be a result of receding sea ice leading to stronger storm surges on the Beaufort Coast, or a result of backwater effects in the delta driven by an interaction between the sea level rise and river discharge, or some combination of the two possibilities. Regardless of the cause, these enhanced water levels should be affecting the long-term thermal balance of permafrost and the sediment mass balance of the delta [Syvitski, 2002], and in particular, the loss of sediment at the coastal margin. River discharge is at relatively low levels during this period (September–November) when the delta appears to be exchanging higher than historical amounts of water with the river. Consequently, this could have localized effects on the nutrient regime in coastal waters of the Beaufort Sea.

[43] An important general issue is how Mackenzie River discharge and channelized nutrient transport may eventually respond to climate warming. One review [Rouse et al., 1997] has argued that Mackenzie runoff should decline even if precipitation within the basin increased modestly, because more energy would be available for evapotranspiration and soil moisture storage within the basin would become enhanced though the lowering of the permafrost table. On the other hand, recent analyses of long-term records for Russian rivers show discharges have increased 6–8% since the 1930s, with the Mackenzie not necessarily fitting this pattern [Peterson et al., 2002, 2006]. Our analysis in the present paper is based on the assumption that Mackenzie River discharge has not changed significantly over the period of record [Woo and Thorne, 2003]. Changes in discharge would have complex effects on nutrient fluxes.

#### 4.5. Use of the Nutrient Flux Estimates

[44] Whereas the nutrient fluxes we have reported (Table 2) represent the hydrograph recession period rather than a full year, the estimates are based on the most frequent and complete sampling that has been thus far done over the open water period for the Mackenzie gauging stations immediate-

ly upstream of the delta. Our data set includes results from a more complete temporal sampling of the Mackenzie River by comparison with the Environment Canada database, and it includes data from the high-discharge, early recession phase of the hydrograph. Additionally, our mixing model results, in combination with the channel network nutrient surveys, have provided a means to estimate the scale of the delta effect on nutrient fluxes at the downstream end of the delta, and to assess the representativeness of nutrient concentrations reported for distributary channels of the lower delta, where water discharges are not generally gauged. Prior Mackenzie flux estimates have been derived from less complete data sets and can be split into results from two regions of the delta: (1) the Mackenzie River proper (supplemented by Arctic Red and Peel rivers) upstream of the delta where discharge has been continuously monitored since 1973; and (2) spot measurements in various ungauged distributary channels.

[45] Upstream of the delta, the longest available nutrient record (1971–2001) is that of Environment Canada (2001) for the Mackenzie gauging station at Arctic Red River (Table S2). This database includes concentrations (typically monthly, or less than monthly) of various nutrients, contaminants, DOM, particulates, and some heavy metals. Monthly measurements of various nutrient and DOM constituents from 2 years during the early 1980s is also available from *Telang et al.* [1991]. Several other studies are cited in Table S2; however, they are not broadly comparable to this study because of considerable differences in location, time of year, and methodology.

[46] There are a variety of data from spot measurements in various distributary channels (Table S2); however, there has been no objective way to derive a representative concentration for total Mackenzie River discharge from these measurements. For example, comprehensive measurements of nutrients and particulates were made by *Brunskill et al.* [1973] over 2 years in five ungauged delta channels. Environment Canada's (2001) database also includes results from three delta channels over 2 years but with only a limited suite of measurements. Other studies have concentrated on nutrient patterns in specific delta channels over short periods.

[47] Among particulate measures, our results relative to the Environment Canada database are higher for POC and PP, roughly same for PN and lower for TSS. Work by *Carson et al.* [1998] is generally the accepted estimate of suspended sediment load to the Arctic Ocean ( $124 \text{ Mt a}^{-1}$ ) from the Mackenzie Delta [*Holmes et al.*, 2002] and provides a more precise estimate of TSS than the Environment Canada database. This was a sophisticated effort involving the Environment Canada 1-D hydraulic model and other techniques specifically to estimate sediment transport through the delta. We emphasize the results of Carson et al. strongly support our premise that the delta effect on Mackenzie River particulates shown in our results would be substantially stronger if we had nutrient data for the rising discharge period. For example, Carson et al. estimated Mackenzie sediment fluxes of  $90 \text{ Mt a}^{-1}$  June–October, but  $124 \text{ Mt a}^{-1}$  when the May breakup period is included. Among dissolved constituents, our results relative

to prior reports are generally lower for TDOC and SRP, whereas  $\text{NO}_3^-$  and SRSi are roughly similar. Among composite measures, our results are generally lower for TDN, TDP, and TP and similar for TOC. The overall suite of differences in our results relative to prior work yields a set C:N:P ratios that differ markedly from prior reports for the Mackenzie River. Our results here extend beyond earlier work by capturing the effect of the delta on particulates and dissolved nutrients, and have resulted in improved estimates of organic carbon and nutrient delivery to the coastal Beaufort Sea.

## 5. Conclusions

[48] The results from our two-source mixing model, incorporating channel water plus recovery of water stored off-channel in the delta through the hydrograph recession period, indicate that the Mackenzie Delta has an appreciable effect on riverine nutrient fluxes to the Arctic Ocean. These modeling results were reasonably consistent with our upstream-downstream comparisons of nutrient content in the channel network, though the lumped-effect model does not capture time-dependent features of the delta effect. More specifically, river water entering the ocean appears to be enriched (relative to concentrations upstream of the delta) in DON and DOP, but depleted in particulates and some inorganic nutrients to a point that appreciably affects the C:N:P ratio of the water mass. The effect of particle stripping from river water by the delta was substantial, even though the period of comparison did not include the rising water phase. This effect would likely be stronger if quantified through a complete annual cycle of river discharge. Relative to prior nutrient concentrations published for the Mackenzie, our modeling approach here has captured the effect of the delta on river water particulates plus dissolved nutrients and DOM. Our results have improved estimates of the carbon, nitrogen and phosphorus composition of Mackenzie River water, ultimately leading to improved estimates of C, N and P fluxes and their stoichiometry.

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